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CHEMICAL AND PHOTOCHEMICAL REACTIONS OF PORPHYRINS AND
METALLOPORPHYRINS I. (U) NORTH CAROLINA UNIV AT CHAPEL
HILL DEPT OF CHEMISTRY D G WHITTEN 15 FEB 84
ARO-14502. 4-CH DAAG29-80-K-0066

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1. REPORT NUMBER ARO 14502.4-CH ; ARO 17080.4-CH	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Chemical and Photochemical Reactions of Porphyrins and Metalloporphyrins in Micelles, Vesicles, Films, Monolayer Assemblies and Solution.	5. TYPE OF REPORT & PERIOD COVERED Final Report Jan. 1977 - Sept. 1983
7. AUTHOR(s) David G. Whitten	6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of North Carolina at Chapel Hill Chapel Hill, North Carolina 27514	8. CONTRACT OR GRANT NUMBER(s) DAAG29 77 G 0063 and DAAG29 80 K 0066
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	12. REPORT DATE February 15, 1984
	13. NUMBER OF PAGES 10
	15. SECURITY CLASS. (of this report) Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.	
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) S B	
18. SUPPLEMENTARY NOTES The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation	
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Porphyrins, Metalloporphyrins, Photooxidation, Singlet Oxygen, Micelles, Photochemistry, Photoatropisomerism, Protoporphyrin IX, Photoporphyrin, Interfacial Reactivity.	
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report describes a number of related studies which center around the general theme of porphyrin photo-reactivity. A number of the studies have focused especially on photoreactions of porphyrins and their metal complexes in organized or interfacial media such as micelles, vesicles or thin films. Reactions investigated have included metal ion incorporation, ligand photoejection, photoatropisomerization and photooxidation of porphyrins. The most extensively investigated reaction has been the last of these; this reaction has been extensively investigated in both solution and organized media with respect to products formed, efficiency of reaction and mechanisms involved.	

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CHEMICAL AND PHOTOCHEMICAL REACTIONS OF PORPHYRINS AND METALLOPORPHYRINS
IN MICELLES, VESICLES, FILMS, MONOLAYER ASSEMBLIES AND SOLUTION

FINAL REPORT

DAVID G. WHITTEN

FEBRUARY 15, 1984

U. S. ARMY RESEARCH OFFICE

DAAG29 77 G 0063 and DAAG29 80 K 0066

DEPARTMENT OF CHEMISTRY
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STATEMENT OF THE PROBLEM STUDIED

The research covered by these two contracts extending over a little more than six years has focused mainly on an investigation of a reactivity of several different types of porphyrins in a variety of different microheterogeneous media. The investigations have been focused along two closely interrelated lines. First we have sought to determine how reactivity can be modified or modulated by change or control of its microenvironment. Secondly by studying a certain characteristic reaction of a molecule in several different media we have simultaneously tried to determine information as to what precise kind of microenvironment the medium provides. In these particular studies, as the title indicates, the molecules under investigation have been porphyrins and their metal complexes, metalloporphyrins. The porphyrin chromophore is an attractive one for investigation since it has characteristic spectroscopic properties which make porphyrins easily detectable even at very low concentrations and furthermore the porphyrin exhibits a variety of interesting and important chemical and biochemical reactions. Among these are both thermal and photochemical processes. Our investigations have been fairly far reaching so as to include a variety of photochemical and thermal reactions of the porphyrins and their metal complexes.

SUMMARY OF THE MOST IMPORTANT RESULTS

Metal Ion Incorporation into Free-Base Porphyrins.

The incorporation of metals into porphyrins is an interesting process which has important biochemical implications; it is a reaction which has been very well studied in homogeneous solutions. Thus it has been found in a number of investigations that a variety of divalent metal ions can be incorporated into various free-base porphyrins in rates which strongly depend on the specific metal involved. Our investigations focused on metal ion incorporation into surfactant free-base porphyrins incorporated into films at the air-water interface or transferred films deposited as multilayer assemblies on various types of hydrophobic and hydrophilic supports. We completed a fairly elaborate study of these metallation reactions and found a remarkable effect on the rate (or even occurrence) of metallation dependent upon the site of the porphyrin, i.e. hydrophobic or hydrophilic. Thus when the porphyrin chromophore was positioned directly at the interface or in an otherwise hydrophilic site, metallation was found to occur very rapidly while other porphyrins, "hidden" in hydrophobic sites, were completely resistant to metal ion incorporation even under very long exposure. We furthermore observed interesting variations in the relative reactivity of different metal ions towards the porphyrins in the films and assemblies compared to homogeneous solutions. Though we have published the key results of our findings, the results obtained are interesting enough to have stimulated additional work in other laboratories and very likely future work in our own.

Ligand Photo Ejection Processes in Supported Multilayers.

Metalloporphyrins readily bind a variety of axial ligands to coordination sites above and below the plane of the porphyrin ring. These ligands often exchange thermally in solution but in many cases even ligands which can not be exchanged thermally can be labeled photolytically. In the solution phase the vacant sites liberated by loss of ligand are rapidly captured unselectively by any ligands available in the bulk solution. We reasoned that in supported multilayers metalloporphyrins prone to ligand photo ejection would not have access to new ligands such that highly reactive porphyrin complexes with free coordination sites could be prepared. We found that this is indeed possible with iron and ruthenium porphyrins and we found that the reactive intermediates prepared by photoejection from photoejection of ligands from the metal complexes could

capture normally unreactive molecules such as molecular nitrogen. We found that more reactive gaseous molecules could be captured and in several cases either reversible or irreversible coordination could be observed.

Photoatropisomerization of Porphyrins.

In our design of suitable surfactant porphyrins for incorporation into a variety of microheterogeneous media, we took advantage of the availability of substituted tetraphenyl porphyrins containing various hydrophobic side chains anchored at the ortho position of the bridge-substituting phenyl groups. These porphyrins exist as various "atropisomers" by virtue of the restricted rotation around the single bond between the phenyl ring and porphyrin macrocycle. For our use in surfactant assemblies, the so-called "picket fence" or (4,0) isomer is most useful. The various atropisomers can be equilibrated thermally and it is normally fairly straightforward to separate out the (4,0) isomer. In the course of our investigations we observed that the various atropisomers are also interconvertible by irradiation into the visible absorption bands of the porphyrin. This reaction proved to be extremely interesting in that it is first of all a novel photochemical process and secondly an interesting one in that four identical reactive centers are present simultaneously and there exists the question of possible multiple site reactivity per single act of photoexcitation. Our study in fact demonstrated that in some cases the photochemical reaction may involve multiple isomerization events per photon while in other cases the reaction is clearly a one bond - one photon process. We were able to complete a fairly comprehensive investigation of this interesting photochemical reaction. In addition to its intrinsic interest we found that the reaction does indeed offer an interesting way of comparing solution properties of the porphyrins with those inferred or determined from X-ray crystal structures.

Photooxidation of Protoporphyrin and Related Porphyrins in Solution and in Organized Media.

Protoporphyrin IX, the key porphyrin in mammalian hemoglobin and cytochromes, as well as in other biological systems, is a good sensitizer for excited singlet molecular oxygen. The porphyrin is also degraded by light in the presence of oxygen to form ultimately a green photo product, "photoproteoporphyrin." The structure of photoproteoporphyrin was determined several years ago by workers in Germany. We decided to investigate the selfsensitized photooxidation of protoporphyrin IX in different microheterogeneous media with specific emphasis on the

mechanisms for photooxidation and the relative ease of forming the green photoproduct. We were also interested in determining the stability of the green photoproduct to subsequent bleaching on exposure to visible light. Interestingly the green photoproduct has an absorption and fluorescent spectra which are quite similar to those of natural chlorophylls. One of our first key findings was that in addition to the green photoproducts there are indeed other porphyrin photooxidation products formed from irradiation of protoporphyrin in the presence of molecular oxygen. While these products are only of minor importance upon irradiation in homogeneous solution, we found that these products become the major products in several microheterogeneous media, especially monolayer films and supported multilayer assemblies. We investigated thoroughly the mechanisms for photooxidation of protoporphyrin IX in solution and found that while most of the reaction can be accounted for by a singlet oxygen mechanism, protoporphyrin IX and several other porphyrins and their metal complexes are also excellent for photogenerating superoxide anion by a photochemical electron transfer process. The reaction of superoxide with the concomitantly formed porphyrin cation radical can lead to the formation of different products from the porphyrin, not including the green "photoprotoporphyrin." We found upon shifting our focus to the various microheterogeneous media that in many cases reactivity here is clearly mechanistically more complicated. Thus, for example, in micelles we find that there are at least three mechanisms for the selfsensitized photooxidation of protoporphyrin IX. In vesicles and microemulsions similar multiple paths for reaction exist. Our investigations in this area have been quite fruitful so far but are still under way and suggest that the various photooxidation reactions initiated by light absorption in various porphyrins can lead to a variety of different reactions which are strongly dependent both on the medium and various substrates available for reaction with various activated forms of molecular oxygen.

LIST OF ALL PUBLICATIONS AND TECHNICAL REPORTS PUBLISHED

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- 2) B. E. Horsey; D. G. Whitten "Environmental Effects of Photochemical Reactions: Contrasts in the Photooxidation Behavior of Protoporphyrin IX in Solution, Monolayer Films, Organized Monolayer Assemblies, and Micelles" J. Am. Chem. Soc. 1978, 100, 1293.
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LIST OF ALL PARTICIPATING SCIENTIFIC PERSONNEL

<u>Individual</u>	<u>Status While at UNC</u>	<u>Degree Awarded</u>	<u>Present Position</u>
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William A. Mooney	Graduate student	PhD	Postdoctoral researcher at Saclay, France
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Carol Sutcliffe	Graduate student	MS	Laboratory investigator at Los Alamos
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Marianne Krieg	Postdoctoral fellow	none	Postdoctoral fellow working on an extension of this project

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